Electron Impact Induced Fragmentation of Alkyl(benzylidene)amines

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The mass spectral decomposition reactions of alkyl(benzylidene)amines (Schiff's bases) have been investigated with the aid of deuterium labelling, high resolution measurements, and metastable defocusing. The most significant results are (a) cleavage of the C(4)–C(5) bond (δ-cleavage) with formation of five-membered ring fragment ions is very much favoured over other C–C bond fissions; (b) very abundant $C_7H_7^+$ ions are formed through skeletal rearrangement processes, joining the phenyl group to the α-methylene group of the alkyl fragment; and (c) very abundant ($M - C_6H_5$) and ($M - C_6H_6$) ions are formed at low voltage from benzylidene(butyl)amine and the labelled analogues, the C_6H_6 neutral fragment eliminated incorporating the methine hydrogen atom. Ring closure is suggested to accompany the formation of both ions; similar fragmentations take place to a much lesser extent in the fragmentation of other alkylimines.

THE mass spectrometry of nitrogen-containing derivatives of aldehydes and ketones has received considerable attention in the last decade.[1] Among these, alkylimines of aliphatic aldehydes and ketones have been investigated thoroughly,[2,3] as have anils of aromatic aldehydes.[4] Only one report has appeared, however, on the mass spectral fragmentations of alkylimines of aromatic aldehydes, namely five alkylimines of pyridine-2-carbaldehyde.[5] The major pathway of fragmentation was reported to be α-cleavage in the alkyl group, and subsequent elimination of an HCN neutral molecule, generating the pyridine analogue of the benzyl or tropylium ion. This process was suggested to occur *via* hydrogen transfer from the alkyl α-carbon atom, since the one secondary alkylimine examined, $C_5H_4NCH{=}NCHMe_2$, eliminated MeCN rather than HCN subsequent to α-cleavage.

Recently, a number of reports have appeared [6] dealing with the formation of abundant $C_7H_7^+$ ions *via* elimination of hetero-fragments in skeletal rearrangements of the type $C_6H_5{-}X{-}Y{-}CH_2^+ \longrightarrow C_6H_5CH_2^+ + XY$. The mechanism for these reactions is of necessity different from that suggested by Schumacher and Traubenest,[5] since a new C–C bond must be formed where X is different from carbon, and we therefore found it of interest to investigate more closely the mechanism of formation of the $C_7H_7^+$ species from alkylimines of aromatic aldehydes to see if, in fact, a similar process was taking place. We have examined the mass spectra of benzylidene(butyl)amine and six deuterium labelled analogues, and a number of other primary, secondary, and tertiary alkylimines; the compounds are listed in Tables 1 and 2.

TABLE 1

Alkyl(benzylidene)amines examined

	Alkyl		Alkyl
(I)	Pr^n	(VI)	n-C_5H_{11} [a]
(II)	Pr^i	(VII)	$MeCHPr^n$
(III)	Bu^n [a]	(VIII)	n-C_6H_{13}
(IV)	Bu^s	(IX)	$MeCH$-n-C_5H_{11}
(V)	Bu^t [a]	(X)	n-$C_{10}H_{21}$

[a] *Cf.* Table 2.

TABLE 2

Deuterium labelled alkyl(benzylidene)amines

(IIIb)	$C_6D_5CD{=}N[CH_2]_3Me$
(IIIc)	$C_6H_5CD{=}N[CH_2]_3Me$
(IIId)	$C_6H_5CH{=}NCD_2[CH_2]_2Me$
(IIIe)	$C_6H_5CH{=}NCH_2CD_2CH_2Me$
(IIIf)	$C_6H_5CH{=}N[CH_2]_2CD_2Me$
(IIIg)	$C_6H_5CH{=}N[CH_2]_3CD_3$
(Vb)	$C_6H_5CD{=}NCMe_3$
(VIb)	$C_6H_5CH{=}NCD_2[CH_2]_3Me$
(VIc)	$C_6H_5CH{=}NCH_2CD_2[CH_2]_2Me$
(VId)	$C_6H_5CH{=}N[CH_2]_2CD_2CH_2Me$

RESULTS AND DISCUSSION

The principal peaks in the mass spectra of Schiff's bases of benzaldehyde are collected in Tables 3 and 4. The 70 eV molecular ions are of intermediate intensity, decreasing with increasing chain length, and are in nearly all spectra accompanied by slightly more intense ($M - 1$) peaks. The hydrogen atom lost in the formation of the corresponding ion is either the methine hydrogen or an aromatic proton, as shown by the ($M - 2$) peaks in the spectra of (IIIb) and (IIIc). Elimination of a ring hydrogen atom implies cyclisation, but none of the fragment ions have been found to be formed *via* this ion.

α-Cleavage.—The two most intense peaks in most of the 70 eV spectra of lower alkyl(benzylidene)amines (*i.e.* amines with terminal methyl groups no more than four carbon atoms removed from the nitrogen atom) correspond formally to ions formed through α-cleavage and

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[1] H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, ch. 10.

[2] M. Fischer and C. Djerassi, *Chem. Ber.*, 1966, **99**, 1541.

[3] W. Carpenter, A. M. Duffield, and C. Djerassi, *J. Amer. Chem. Soc.*, 1967, **89**, 6167.

[4] D. J. Elias and R. G. Gillis, *Austral. J. Chem.*, 1966, **19**, 251; J. H. Bowie, R. G. Cooks, J. W. Fisher, and T. McL. Spotswood, *ibid.*, 1968, **21**, 2021; J. H. Bowie and P. J. Hoffmann, *ibid.*, 1969, **22**, 1219; D. J. Elias and R. G. Gillis, *ibid.*, p. 2249.

[5] E. Schumacher and R. Traubenest, *Helv. Chim. Acta*, 1966, **49**, 1455.

[6] I. R. McKinley and H. Weigel, *Chem. Comm.*, 1970, 1022; R. J. Bose and M. D. Peters, *Canad. J. Chem.*, 1971, **49**, 1766; C. Cone, M. J. S. Dewar, R. Golden, F. Maseles, and P. Rona, *Chem. Comm.*, 1971, 1522; R. H. Cragg, K. J. A. Hargreaves, J. F. J. Todd, and R. B. Turner, *ibid.*, 1972, 336.

through subsequent elimination of HCN from the α-cleavage product.

C–C Bond cleavage α to the nitrogen atom is known also to give rise to very abundant ions in the decomposition of alkylamines,[7] *N*-alkylamides,[8] and aliphatic Schiff's bases.[2,3]

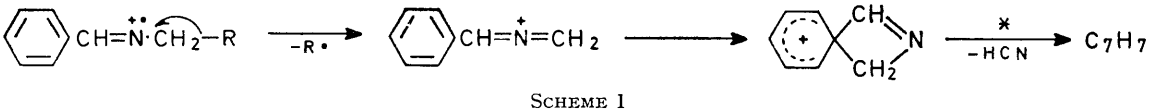
TABLE 3

Mass spectra of benzylidene(butyl)amine and labelled analogues [a,b]

	(IIIa)	(IIIb)	(IIIc)	(IIId)	(IIIe)	(IIIf) [c]	(IIIg) [d]
M	161 (15, 60) 160 (18, 55)	167 (31, 74) 166 (7, 10) 165 (13, 23)	162 (20, 69) 161 (7, 15) 160 (7, 17)	163 (18, 60) 162 (20, 54)	163 (17, 64) 162 (20, 59)	163 (19, 50) 162 (28, 65) 161 (8, 19)	164 (17, 59) 163 (21, 58)
$M - C_1$	146 (2, 3)	152 (3, 3)	147 (2, 3)	148 (1, 2) 147 (1, 2) 146 (1, 2)	148 (2, 3)	148 (2, 3)	147 (1, 2) 146 (1, 2)
$M - C_2$	133 (9, 15) 132 (27, 36)	139 (7, 9) 138 (27, 22) 137 (17, 6) 136 (2, -) 135 (2, -)	134 (7, 12) 133 (30, 32) 132 (3, 2)	135 (4, 5) 134 (13, 7) 133 (10, 13) 132 (8, 10) 131 (2, -)	135 (4, 7) 134 (21, 22) 133 (5, 8) 132 (9, 12)	135 (2, 4) 134 (9, 12) 133 (9, 12) 132 (30, 32)	136 (-, 3) 135 (3, 3) 134 (6, 10) 133 (17, 20) 132 (4, 5)
$M - C_3$	120 (6, 19) 119 (36, 100) 118 (100, 76) 117 (8, 2)	126 (7, 11) 125 (45, 74) 124 (78, 34) 123 (69, 15) 122 (11, 2)	121 (5, 13) 120 (34, 84) 119 (100, 53) 118 (10, 3)	122 (5, 11) 121 (34, 81) 120 (100, 48) 119 (16, 20) 118 (6, 3)	121 (-, 3) 120 (7, 23) 119 (36, 91) 118 (100, 52) 117 (8, 2)	121 (4, 7) 120 (24, 52) 119 (64, 59) 118 (74, 52) 117 (8, 2)	122 (2, 6) 121 (4, 10) 120 (8, 19) 119 (40, 100) 118 (100, 72) 117 (7, 3)
$M - C_4$	105 (10, 4) 104 (33, 9)	111 (11, -) 110 (9, -) 109 (28, 3)	106 (8, -) 105 (6, -) 104 (21, 4)	106 (4, 2) 105 (12, 2) 104 (32, 6)	106 (4, 2) 105 (12, 2) 104 (26, 6)	106 (7, 10) 105 (20, 8) 104 (37, 11)	106 (6, 3) 105 (14, 6) 104 (17, 3)
$M - C_4N$	92 (8, -) 91 (87, 2) 90 (8, -) 89 (9, -)	97 (18, -) 96 (100, 3) 95 (10, -) 94 (10, -)	92 (16, -) 91 (86, 2) 90 (9, -) 89 (3, -)	94 (8, -) 93 (86, 2) 92 (8, -) 91 (9, -) 90 (6, -) 89 (6, -)	92 (10) 91 (83, 2) 90 (8, -) 89 (9, -)	92 (12, -) 91 (100, 7) 90 (10, -) 89 (11, -)	92 (7, -) 91 (74. 5) 90 (7, -) 89 (8, -)
M – aryl	84 (34, 98) 83 (24, 91)	85 (56, 100) 84 (10, 11) 83 (32, 66) 82 (14, -) [e]	85 (37, 100) 84 (4, 13) 83 (17, 61)	86 (37, 100) 85 (26, 92)	86 (33, 99) 85 (25, 100) 84 (2, 7)	86 (39, 87) 85 (40, 100) 84 (11, 26)	87 (29, 90) 86 (21, 79)

[a] All peaks >2% rel. int. above *m/e* 80 included, except for natural-abundance isotope peaks. [b] Given as *m/e* (rel. int. 70 eV, rel. int. 12 eV). [c] 80% $^2H_2$, 20% $^2H_1$. [d] 92% $^2H_3$, 8% $^2H_0$; where obvious, the $^2H_0$ peaks have been omitted. [e] C_6D_5.

The elimination of HCN takes place by a skeletal rearrangement (Scheme 1), as shown by the spectra of the [*methine*-^{2}H] (IIIc) and [α,α-$^2H_2$] compounds (IIId) and (VIb). The ion from α-cleavage of the former eliminates DCN with formation of $C_7H_7^+$ ions, and the ions from α-cleavage of the latter two expel HCN with formation of $C_7H_5D_2^+$. The benzyl or tropylium ions are consequently made up by union of the α-methylene part of the alkyl group and the phenyl group. This is further supported by the formation of higher homologues of the $C_7H_7^+$ ion by HCN elimination from the α-cleavage products of the secondary alkylimines (II), (IV), (VII), and (IX) (see below). Similarly, butyl-(α-methylbenzylidene)amine eliminates an MeCN fragment subsequent to α-cleavage; the $C_7H_7^+$ ions thus formed give rise to the base peak in the spectrum of this compound.[9] The HCN (DCN, MeCN) expulsion processes also give rise to very intense metastable peaks of approximately Gaussian shape. It is interesting to note that these reactions proceed without significant H–D exchange between ring and side chain positions (scrambling), even in the decompositions taking place in the second field-free region. Neither the spectra of (IIIc) nor of (IIId) or (VIb) show significant metastable peaks corresponding to elimination of HCN (DCN) after scrambling (Table 5).



SCHEME 1

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[7] R. S. Gohlke and F. W. McLafferty, *Analyt. Chem.*, 1962, **34**, 1281.

[8] Z. Pelah, M. A. Kielczewski, J. M. Wilson, M. Ohashi, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.*, 1963, **85**, 2470; A. M. Duffield, H. Budzikiewicz, and C. Djerassi, *ibid.*, 1965, **87**, 2913.

[9] S. Hammerum, unpublished results.

TABLE 4

Mass spectra of alkyl(benzylidene)amines [a,b]

Mass	(X)	(VIII)	(VI)	(I) [h]	(IX)	(VII)	(IV)	(II)	(V)
245	(4, 5)								
244	(5, 2)								
230	(2, -)								
216	(3, 2)								
203					(4, 4)				
202	(5, 3)				(5, 2)				
189		(5, 5)			(3, 2)				
188	(7, 3)	(7, 3)			(14, 8)				
175	(3, 2)		(10, 11) [c]		(15, 15)	(5, 13)			
174	(18, 7)	(10, 3)	(16, 10) [c]		(98, 100)	(7, 9)			
168	(4, 2)								
161	(14, 14)	(13, 13)	(10, 14) [c]		(4, 3)	(7, 13)	(4, 10)		(19, 38)
160	(100, 100)	(98, 100)	(71, 100) [c]		(10, 6)	(49, 100)	(6, 9)		(5, 4)
147	(3, 2)	(3, 2)	(3, 2) [d]	(9, 49)	(8, 5)	(2, 2)	(4, 8)	(52, 100)	(12, 13)
146	(8, 3)	(13, 5)	(13, 6) [d]	(23, 100)	(20, 2)	(6, 4)	(29, 60)	(11, 5)	(100, 100)
134						(12, 7)	(5, 7)		
133	(10, 4)	(13, 5)	(19, 13) [e]		(33, 15)	(34, 46)	(15, 22)	(11, 6)	
132	(31, 7)	(54, 13)	(66, 21) [e]	(3, 2)	(100, 16)	(100, 50)	(100, 100)	(100, 55)	
126						(4, 3)			
120	(15, 7)	(14, 7)	(17, 11) [f]	(3, 8)		(3, 4)			
119	(25, 10)	(29, 12)	(30, 16) [f]	(21, 67)	(2, -)	(2, 2)			
118	(45, 3)	(88, 8)	(99, 11) [f]	(75, 44)	(5, -)	(5, -)			
117	(12, 2)	(22, 3)	(15, 3) [f]	(7, -)	(5, -)	(6, 2)	(3, -)	(3, -)	
112		(6, 3)							
106	(14, 4)	(12, 3)	(10, 3)		(17, 3)	(8, 6)	(5, -)	(3, -)	(34, 9) [i]
105	(9, 2)	(18, -)	(24, 2)	(4, -)	(25, -)	(21, 2)	(17, -)	(23, -)	(13, 3) [i]
104	(17, -)	(40, 3)	(50, 5)	(18, -)	(22, -)	(20, 3)	(16, -)	(35, -)	(25, -) [i]
98			(20, 15) [c]				(7, 11)		
97			(9, 13) [c]				(4, 9)		
92	(6, -)	(9, -)	(9, -) [g]	(8, -)	(3, -)				
91	(48, -)	(100, 2)	(100, 2) [g]	(100, 2)	(21, -)	(16, -)	(11, -)	(7, -)	(5, -)
90	(5, -)	(10, -)	(10, -) [g]	(8, -)	(9, -)	(8, -)	(7, -)	(7, -)	(9, -)
89	(4, -)	(10, -)	(10, -) [g]	(12, -)	(7, -)	(8, -)	(7, -)	(8, -)	(8, -)
84							(2, 4)		

[a] All peaks >2% rel. int. above *m/e* 80 given, excluding natural-abundance isotope peaks. [b] Given in % of base peak at 70 and 12 eV. [c] Corresponding peak 2 a.m.u. higher in (VIb—d). [d] *m/e* 148, 147, 146 in (VIb—d) (70 eV): 5,5,9; 5,4,8; 13,2,2. [e] *m/e* 135, 134, 133, 132 in (VIb—d) (70 eV): 12,37,30,12; 14,58,10,10; 5,23,79. [f] *m/e* 122, 121, 120, 119, 118, 117 in (VIb—d) (70 eV): 18,30,100,16,11,2; 2,16,34,100,11; 11,21,53,53,15. [g] *m/e* 94, 93, 92, 91, 90, 89 in (VIb) (70 eV): 8,89,10,21,6,6. [h] *m/e* 70: (8,32) *m/e* 69: (1,3). [i] *m/e* 107, 106, 105, 104 in (Vb) (70 eV): 32,11,5,18.

These results do not conform with the data presented by Schumacher and Traubenest[5] for alkylimines of pyridine-2-carbaldehyde. Preliminary experiments with labelled and unlabelled alkylimines of pyridine-2-, -3-, and -4-carbaldehydes confirm the results of the previous authors, but also indicate that the behaviour described is peculiar to derivatives of pyridine-2-carbaldehyde, possibly because of interaction between the α-carbon atom and the ring nitrogen.

Labelling of the aromatic ring protons reveals that at most half of the ions corresponding in elemental composition to the products of α-cleavage are formed through simple cleavage, since a partial shift of $(M - 43)$ to $(M - 44)$ is observed in the spectrum of (IIIb). The latter arises *via* elimination of an alkene molecule from the molecular ion, followed by loss of a hydrogen (deuterium) atom from the ring, probably by cyclisation as depicted in Scheme 2. This ion does not eliminate HCN to any appreciable extent and must therefore possess a structure quite different from that of the isomeric ion generated in the simple cleavage reaction. Spectra of the various compounds labelled in the alkyl group show that the hydrogen atom rearranged prior to alkene elimination is a δ-hydrogen (see Table 3), and the H rearrangement might then conveniently be described as a McLafferty rearrangement to carbon [path (a) in

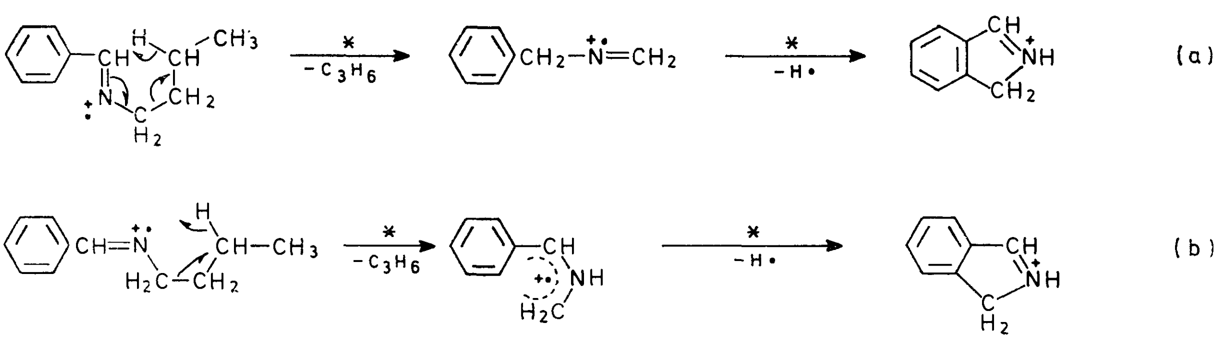
TABLE 5

Metastable peaks in the spectra of benzylidene(butyl)-amine and labelled analogues [a]

Peak	Reaction	Peak [c]	Reaction [c]	Compd. [c]
159·0	161 $\longrightarrow$ 160	163·1	167 $\longrightarrow$ 165	(IIIb)
108·2 [b]	161 $\longrightarrow$ 132	108·5 [b]	163 $\longrightarrow$ 133	(IIId)
		106·9 [b]	163 $\longrightarrow$ 132	(IIId)
		110·1	163 $\longrightarrow$ 134	(IIIe)
		107·0	163 $\longrightarrow$ 132	(IIIe)
		109·5	164 $\longrightarrow$ 134	(IIIg)
		107·9 [b]	163 $\longrightarrow$ 133	(IIIg)
88·0 [b]	161 $\longrightarrow$ 119	88·4	163 $\longrightarrow$ 120	(IIIf)
		86·2 [b]	164 $\longrightarrow$ 119	(IIIg)
43·8 [b]	161 $\longrightarrow$ 84	43·2 [b]	167 $\longrightarrow$ 85	(IIIb)
42·8 [b]	161 $\longrightarrow$ 83	41·2 [b]	167 $\longrightarrow$ 83	(IIIb)
		42·5 [b]	162 $\longrightarrow$ 83	(IIIc)
131·0	133 $\longrightarrow$ 132	135·1	139 $\longrightarrow$ 137	(IIIb)
		133·0	135 $\longrightarrow$ 134	(IIId)
		131·0	133 $\longrightarrow$ 132	(IIId)
83·6 [d]	132 $\longrightarrow$ 105			
117·0 [e]	119 $\longrightarrow$ 118	121·1 [b]	125 $\longrightarrow$ 123	(IIIb)
70·2 [d,e]	118 $\longrightarrow$ 91	74·3 [d,e]	124 $\longrightarrow$ 96	(IIIb)
		69·6 [d,e]	119 $\longrightarrow$ 91	(IIIc)
		72·1 [d,c]	120 $\longrightarrow$ 93	(IIId)
103·0 [d]	105 $\longrightarrow$ 104	107·1 [d]	111 $\longrightarrow$ 109	(IIIb)
		102·1 [d]	106 $\longrightarrow$ 104	(IIIc)
57·0 [d]	104 $\longrightarrow$ 77			
46·4 [d]	91 $\longrightarrow$ 65			

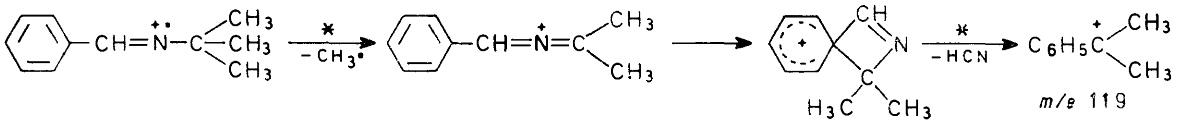
[a] Metastable peak for labelled compounds only included if eliminated fragment incorporates label or if mentioned in text. [b] Increases at low ionising voltage. [c] Labelled compounds. [d] Decreases (disappears) at low ionising voltage. [e] Very intense.

Scheme 2]. However, the loss of a hydrogen atom from the aromatic ring in the subsequent reaction may then require internal migration of a hydrogen atom to nitrogen. An alternative mechanism would be alkene elimination *via* a five-membered transition-state with hydrogen transfer to nitrogen instead [path (b)]. It should be noted that neither the methine proton nor the α-hydrogen atoms are involved to any appreciable extent in these reactions. The 70 eV spectrum of (IIIb) shows that the three ions associated with α-cleavage, ($M - C_3H_6$), ($M - C_3H_6 - D$), and ($M - C_3H_7$), are formed in nearly equal abundance; at low voltage the ($M - C_3H_6$) ion predominates, as is expected for the product of a rearrangement.[10]



SCHEME 2

Benzylideneamines with secondary alkyl groups may undergo α-cleavage by loss of either of the two alkyl fragments bonded to the α-carbon atom. At 70 eV the larger alkyl group is lost preferentially, whereas lowering the ionising voltage leads to increased elimination of the smaller group, in close analogy with what has been observed for amines and other compounds capable of exhibiting competing α-cleavage reactions.[3,11] α-Methylimines do not show the divergent behaviour noted for amines with α-methyl substituents.[11] The relative number of carbon atoms in the two alkyl fragments is important in determining which fragment is lost preferentially, as may be seen from the spectra of benzylidene-(s-butyl)amine (IV) and -(1-methylbutyl)amine (VII). In the 12 eV spectrum of the former, loss of ethyl is still more pronounced than loss of methyl, whereas the peak corresponding to (M — Me) is considerably more intense than the (M — Pr) peak in the 12 eV spectrum of the latter.



SCHEME 3

The ions formed by α-cleavage in the decomposition of secondary alkylimines fragment further in the same manner as the straight-chain homologues, by elimination of an HCN neutral molecule, with formation of hydrocarbon ions. Only the ions corresponding to HCN elimination from the α-cleavage ion formed by loss of the larger alkyl radical give rise to peaks of appreciable intensity, even though metastable peaks are observed in some spectra for both possible modes of HCN loss. This probably reflects in part the greater abundance of the (M — large alkyl) precursors in the 70 eV decomposition, as well as more rapid decomposition of *e.g.* $C_6H_5C_4H_8^+$ than of $C_6H_5C_2H_4^+$. Another contributing factor may be the relative bulk of the two alkyl groups, causing these to interfere to a different extent with the C–C bond formation preceding HCN expulsion (see below).

α-Cleavage with H rearrangement occurs also in secondary alkylamines, and becomes increasingly important at low ionising voltage, even though the corresponding peaks do not become more intense than those corresponding to ' simple ' cleavage.

The mass spectra of benzylidene-(t-butyl)amine (Va) and of the [*methine*-^{2}H]analogue (Vb) show α-cleavage as the most important fragmentation reaction in the decomposition of these compounds. Elimination of HCN (DCN) from the α-cleavage ions would give rise to ions of *m/e* 119, but the corresponding peaks are barely visible in the spectra. A very intense flat-topped metastable peak corresponding to this reaction is nonetheless observed in the spectra of both. The width of this, as determined from spectra run at varying accelerating voltages (2, 4, 6, and 8 kV),[12] shows that the elimination of HCN occurs with release of *ca.* 0·85 eV of kinetic energy.

These results are interpreted in terms of a considerable

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[10] R. G. Cooks, I. Howe, and D. H. Williams, *Org. Mass Spectrometry*, 1969, **2**, 137.

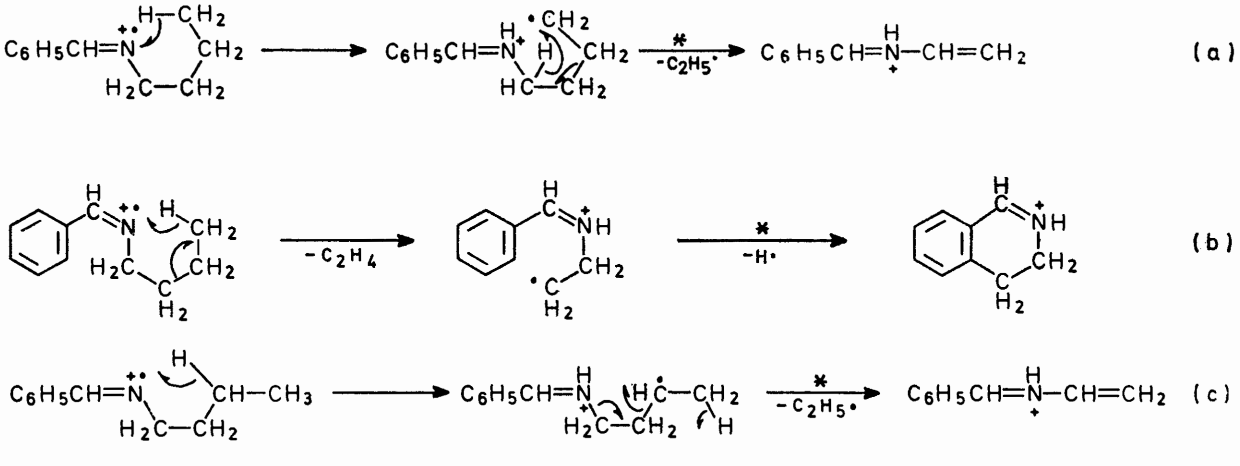
[11] C. A. Brown, A. M. Duffield, and C. Djerassi, *Org. Mass Spectrometry*, 1969, **2**, 625.

[12] J. H. Beynon and A. E. Fontaine, *Z. naturforsch.*, 1967, **22a**, 334.

kinetic shift for the HCN expulsion process. Appreciable kinetic shifts are usually observed when the rate constant for the process under consideration rises only slowly with increased internal energy, which is the case for many rearrangements. In the present case it has not been possible to estimate the magnitude of the kinetic shift, since the appearance potential of an ion of no more than 0·5% relative abundance is difficult to determine. The reason for the large kinetic shift is believed to be the steric bulk of the two methyl groups, causing a very low frequency factor for the bond formation. Also, a high activation energy for this process would contribute to the magnitude of the kinetic shift. The kinetic energy released in the metastable decomposition shows that the back reaction has a considerable energy of activation.

α-Cleavage with hydrogen rearrangement is not possible in the t-butylimines. Instead, these compounds undergo cleavage of the alkyl–nitrogen bond, with concomitant transfer of two hydrogen atoms, forming $C_6H_5CH{=}NH_2^+$ ions. Similar processes do not give rise to peaks of appreciable intensity in spectra of other Schiff's bases.

β-*Cleavage.*—β-Cleavage in the alkyl group gives rise to fairly intense peaks in the spectra of Schiff's bases with straight chain alkyl groups (30—70% rel. int.), whereas the corresponding peaks in secondary alkylimines are somewhat less intense. These ions cannot be formed by ' simple cleavage ' of the C(2)–C(3) bond, since there is no appreciable ($M - C_2H_2D_3$) peak in the spectrum of (IIIg); close examination of the spectra of the labelled alkylimines reveal that a number of distinct processes contribute to the formation of these ions, either proceeding *via* reciprocal * hydrogen transfer reactions or *via* stepwise elimination of an alkene fragment and a hydrogen atom. Mechanistic rationalisations for these processes are depicted in Scheme 4.



SCHEME 4

TABLE 6

Relative abundance of $(M - C_6H_5)^+$ and $(M - C_6H_6)^{+\cdot}$ ions at 12 eV

Alkyl	$(M - C_6H_5)^+$	$(M - C_6H_6)^{+\cdot}$
Pr	32	
Bu	98 [a]	91 [a,b]
n-C_5H_{11}	15	13
n-C_6H_{13}	3	
n-$C_{10}H_{21}$	2	
Pr^i		
BuS	4	
$MeCHPr^i$	11	9
MeCH-n-C_5H_{11}	3	
Bu^t		

[a] Intensities quite dependent on ionising voltage; variations of ±10% rel. int. observed with ±0·5 V change; similar effects noted for the other compounds examined. [b] Reduced to *ca.* 60% in spectra of [*methine*-^{2}H] compounds [(IIIb) and (IIIc)].

The clearest evidence for process (a) (Scheme 4) is found in the spectra of the [α,α-$^2H_2$]- and [δ,δ,δ-$^2H_3$]-butylimines (IIId) and (IIIg) and the [α,α-$^2H_2$]pentylimine (VIb). The α-deuteriated compounds show loss of an alkyl fragment incorporating one deuterium atom (supported by the appropriate metastable peak, see Table 5), and the δ-deuteriated compound similarly expels an alkyl radical incorporating only two of the three deuterium atoms (also supported by a metastable peak). Processes of a similar nature have been reported to occur prior to the expulsion of alkyl fragments from aliphatic aldehydes,[13] ketones,[14] and oximes.[15] The operation of process (b) is evident from spectra of the unlabelled as well as the labelled compounds, inasmuch as a metastable peak is observed for the elimination of an alkene fragment from the molecular ion. The hydrogen atom migrating prior to (or simultaneously with) this reaction is a δ-hydrogen [loss of $C_2H_2D_2$ in

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* Reciprocal is here not used in the sense that two hydrogen atoms exchange positions, but that a hydrogen atom from the fragment subsequently eliminated has migrated to the charge-retaining portion of the ion, and that another hydrogen atom has migrated from here to the eliminated fragment.

[13] R. Liedke and C. Djerassi, *J. Amer. Chem. Soc.*, 1969, **91**, 6814.

[14] W. Carpenter, A. M. Duffield, and C. Djerassi, *J. Amer. Chem. Soc.*, 1968, **90**, 160; M. Kraft and G. Spiteller, *Annalen*, 1968, **712**, 28.

[15] M. Kraft and G. Spiteller, *Org. Mass Spectrometry*, 1969, **2**, 541.

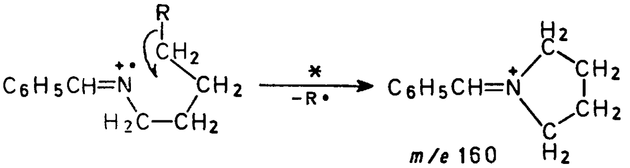
(IIIg)]. The subsequent expulsion of a hydrogen atom from (M — alkene) is assumed to occur with ring closure to the aromatic nucleus, as shown in Scheme 4(b), since a deuterium atom is lost in the fragmentation of (IIIb).

The molecular ion may also eliminate an ethyl radical that incorporates the α- and β-carbon atoms; this reaction leads to ions corresponding to β-cleavage in the butylimine and to γ-cleavage in the pentylimine. The identity of the species lost is confirmed by the observation of (M — $C_2H_3D_2$) peaks and the metastable peaks associated with their formation in the spectra of α- and β-dideuteriated compounds (IIId), (IIIe), (VIb), and (VIc). The mechanism for this reaction may be similar to that suggested by Bernasek and Cooks for loss of ethyl from ethyl butyl ether [process (c) of Scheme 4].[16] It should be noted, however, that the metastable peaks show that at least some of these (M — Et) ions are generated by sequential elimination of C_2H_4 and H•. Elimination of 'inner' alkyl fragments has also been observed to occur in the fragmentation of aldehydes,[13,17] nitriles,[18] and long-chain aliphatic esters.[19]

γ-Cleavage.—This gives rise only to peaks of very low intensity, typically <5% rel. int. Reciprocal hydrogen transfer reactions between the α- and δ-carbon atoms may take place prior to expulsion of the alkyl radical, as demonstrated by the elimination of Me, CDH_2, and CD_2H from (IIId), and of CD_3 and CD_2H, from (IIIg). The 'clean' expulsion of methyl radicals from the remaining labelled butylimines confirms the specificity of the transfer reactions.

δ-Cleavage.—An unexpected feature of the spectra of benzylidene(pentyl)amine and imines with longer alkyl groups is the appearance of an intense peak at m/e 160, corresponding to δ-cleavage, probably with concomitant cyclisation as depicted in Scheme 5.

The formation of this ion is apparently a very favourable process, as witnessed by the intensity of the m/e 160 peak, which is base peak in most 70 eV spectra of imines with alkyl chains of five or more carbon atoms. At low ionising voltages (12 eV nominal) this process is the only one to give rise to peaks of appreciable intensity; the corresponding ions carry more than 50% of the total ion current in the 12 eV spectra of (IX) and (X). It should be noted that elimination of a δ-hydrogen atom from the molecular ion of benzylidene(butyl)amine would correspond to this reaction; such a loss is, however, not observed at all. In the spectra of imines with secondary alkyl groups [*e.g.* (IX)] δ-cleavage at 70 eV gives rise to a peak of approximately the same intensity as that arising from α-cleavage; the low voltage decomposition also leads largely to the δ-cleavage ion (see above).



SCHEME 5

δ-Cleavage reactions leading to very abundant ions have so far only been reported to take place in the decomposition of alkyl bromides and chlorides, and even there only in the absence of α-branching in the alkyl group.[20] McLafferty has, however, presented evidence to show that elimination of alkyl fragments with formation of five-membered ring fragment ions occurs in the decomposition of several other compound types, usually with very low frequency factors.[21] ε-Cleavage in α,β-unsaturated and polyunsaturated esters has been reported to give rise to abundant six-membered ring fragment ions.[22]

Cleavage of Bonds connected directly to the C=N *Group*.—Fission of the nitrogen–alkyl bond of the molecular ion has not been observed to take place to any significant extent in the mass spectral decomposition of the alkylimines. The peak at m/e 104, which corresponds, formally, to the outcome of such a reaction remains unshifted in the spectra of imines labelled at the methine carbon atom (IIIb) and (IIIc), showing that the methine hydrogen is not incorporated in this ion. The m/e 104 peak is, likewise, essentially unshifted in spectra of the α- and β-deuteriated compounds but partially shifted in compounds with deuterium atoms in the γ- and δ-positions. Defocusing experiments have shown that the corresponding ion has several different precursors; formation largely *via* hydrogen transfer to nitrogen, elimination of C_4H_8 followed by loss of the methine proton from the resulting $C_6H_5CH{=}NH^{+\bullet}$ ion is in accord with the labelling results as well as with evidence from metastable ions decomposing in the first and second field free regions.

Fission of the phenyl–carbon bond leads in the fragmentation of benzylidene(butyl)amine to ions corresponding in elemental composition to loss of C_6H_5• and C_6H_6 from the molecular ion. These two ions give rise to peaks that are of intermediate intensity (25—35%) in the 70 eV spectrum but very intense (80—100% rel. int.) in spectra obtained at low voltage. The abundance of these ions varies not only with the ionising voltage, but also with the length of the alkyl group. In spectra of the propyl- and s-butyl-imines only weak peaks corresponding to (M — C_6H_5)$^+$ are observed, and none

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[16] S. L. Bernasek and R. G. Cooks, *Org. Mass Spectrometry*, 1970, **3**, 127.

[17] C. Fenselau, J. L. Young, S. Meyerson, W. R. Landis, E. Selke, and L. C. Leitch, *J. Amer. Chem. Soc.*, 1969, **91**, 6847.

[18] W. Carpenter, Y. M. Shiekh, A. M. Duffield, and C. Djerassi, *Org. Mass Spectrometry*, 1968, **1**, 3.

[19] R. Ryhage and E. Stenhagen in 'Mass Spectrometry of Organic Ions,' ed. F. W. McLafferty, Academic Press, New York, 1963; Ng. Dinh-Nguyen, *Arkiv Kemi*, 1968, **28**, 289; W. Sonnenveld, D. van der Steen, and H. J. J. Pabon, *Rec. Trav. chim.*, 1968, **87**, 1110.

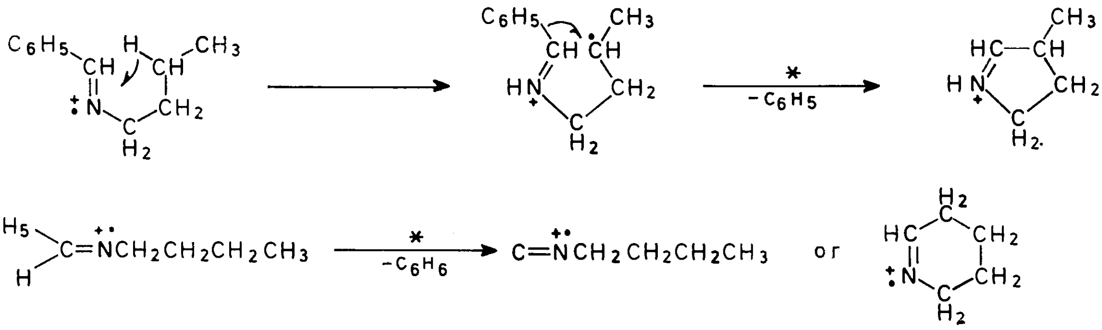
[20] F. W. McLafferty, *Analyt. Chem.*, 1962, **34**, 2.

[21] F. W. McLafferty, D. J. McAdoo, and J. S. Smith, *J. Amer. Chem. Soc.*, 1969, **91**, 5400.

[22] F. W. McLafferty in ref. 19; W. K. Rohwedder, A. F. Mabrouk, and E. Selke, *J. Phys. Chem.*, 1965, **69**, 1711; T. M. Groff, H. Rakoff, and R. T. Holman, *Arkiv Kemi*, 1968, **29**, 179.

corresponding to $(M - C_6H_6)^{+\cdot}$; peaks corresponding to both ions are observed in the spectra of the pentylimines, but in imines with longer alkyl groups only $(M - C_6H_5)^+$ ions are present. The intensity of these peaks also decreases with increasing chain length (Table 6). The cutoff in intensity of both peaks when the carbon chain becomes less than four carbon atoms long suggests that the γ- or δ-carbon atoms are involved in the reactions leading to expulsion of the aryl group; also, the increase in intensity with decreasing ionising voltage suggests that a rearrangement is involved in the genesis of both ions.*

The nature of the rearrangement thought to accompany C_6H_5 loss is not clear, but ring closure to a five- or six-membered ring is assumed (Scheme 6). The $(M - C_6H_6)^{+\cdot}$ ion arises *via* migration of the methine proton to the phenyl group, since exclusive elimination of C_6H_5D is observed in the decomposition of (IIIc); C_6D_6 is correspondingly eliminated from (IIIb). This reaction could, in the absence of further rearrangement, lead to formation of a charged carbene (isonitrile); however, such species are formed very rarely, if at all, in mass spectral decompositions. Formation, rather, of a cyclic ion *via* rearrangement of a δ-hydrogen and formation of a bond between the δ- and methine carbon atoms is believed to take place. The diminished relative intensity of these peaks in low-voltage spectra of imines with larger alkyl groups cannot solely reflect that decomposition by way of δ-cleavage becomes a more favourable reaction, since that would not account for the complete absence of the $(M - C_6H_6)^{+\cdot}$ ions. A satisfactory explanation has, however, not been found.



SCHEME 6

EXPERIMENTAL

The low resolution mass spectra were recorded by Mr. R. Ross on an AEI MS-9 mass spectrometer using the heated inlet system (150 °C) with a source temperature of 200°, and the high resolution mass spectra were obtained by Ms. A. Wegmann on a Varian MAT 711 double-focusing mass spectrometer, also introducing samples *via* the heated inlet system (175 °C). Metastable defocusing experiments were performed on both instruments.[23] Ionising voltage quoted are nominal values only.

The thermal stability of the alkylimines was ascertained by repeated g.l.c. at 200 °C (column temp.) without decomposition; also, thermolysis would be expected to give rise to alkenes, but alkene ions are not prominent in the spectra (<2% rel. int. in all cases).

The alkyl(benzylidene)amines were prepared by treating the appropriate amine with an equimolar amount of benzaldehyde in benzene over freshly dried magnesium sulphate, refluxing for 1—2 h, removing the benzene, and distilling the residue *in vacuo*. The deuterium labelled imines were prepared similarly from appropriately labelled starting materials, and purified by g.l.c. The isotopic purity of the labelled imines was found to be >95% unless otherwise stated below. [$^2H_6$]Benzaldehyde was prepared by chromyl chloride oxidation of [$^2H_8$]toluene.† [*formyl*-^2H]Benzaldehyde was prepared by treatment of benzil with potassium cyanide in deuterium oxide as described by Burgstahler *et al.*[24] [1,1-$^2H_2$]Butylamine and [1,1-$^2H_2$]-pentylamine were prepared by lithium aluminum deuteride reduction of butyronitrile, and valeronitrile, respectively. [2,2-$^2H_2$]Butylamine was prepared from [2,2-$^2H_2$]butyric acid by conversion to the amide and reduction of this with lithium aluminum hydride. [3,3-$^2H_2$]Butylamine was prepared by double exchange of propanal with deuterium oxide–pyridine [25] at 100°, reducing the resulting [2,2-$^2H_2$]-propanal to the alcohol with lithium aluminum hydride, followed by conversion of the propanol to [2,2-$^2H_2$]bromopropane by treatment with triphenylphosphine and bromine in dimethylformamide according to Wiley *et al.*[26] Treatment of the bromopropane with sodium cyanide in dimethyl sulphoxide [27] gave [3,3-$^2H_2$]butyronitrile which was reduced to the amine with lithium aluminum hydride. The benzylideneamine prepared from this contained 80% $^2H_2$ and 20% $^2H_1$. [4,4,4-$^2H_3$]Butylamine was prepared by

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* The variations in relative abundance of the $(M - C_6H_5)^+$ ion with ionising voltage follows the variations in abundance of the ion formed by α-cleavage with hydrogen rearrangement very closely, both increasing at low voltage relative to simple cleavage ions. The formation of the $(M - C_6H_6)^{+\cdot}$ ion already requires that hydrogen migration takes place; it is not possible to use the variations of abundance with ionising voltage to show the occurrence of another rearrangement.

† I thank Dr. K. B. Tomer of this laboratory for a gift of this compound.

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[26] G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, 1964, **86**, 964.

[27] L. Friedman and H. Schechter, *J. Org. Chem.*, 1960, **25**, 877.

alkylating acetonitrile with [2,2,2-$^2H_3$]bromoethane in liquid ammonia.[28] The labelled ethyl bromide was prepared from [$^2H_3$]acetic acid by reduction with lithium aluminum hydride to [2,2,2-$^2H_3$]ethanol and conversion of this to the bromide as given above. The benzylideneamine prepared from this amine consisted of 92% $^2H_3$ labelled and 8% unlabelled material. [2,2-$^2H_2$]Pentylamine was prepared from [2,2-$^2H_2$]bromopentane and hexamethylenetetramine.[29] The labelled bromopentane was prepared as described.[30] [3,3-$^2H_2$]Pentylamine was prepared from [2,2-$^2H_2$]bromobutane by conversion to [3,3-$^2H_2$]valeronitrile as given above, and reduction of the nitrile with lithium aluminum hydride. [2,2-$^2H_2$]Bromobutane was prepared according to Liedke and Djerassi.[13]

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